Supplementary Information for:

Dibenz[a,c]anthracene Derivatives Exhibiting Columnar Mesophases over Broad Temperature Ranges

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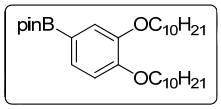
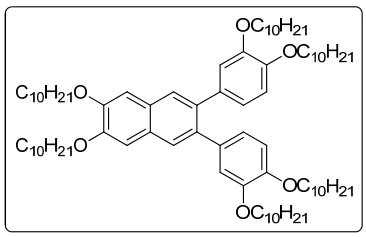
Synthesis

General

^{1}H-NMR and ^{13}C-NMR were recorded using a Varian 300 MHz (^{1}H) Unity Inova NMR Spectrometer, using indicated deuterated solvents purchased from CIL Inc. All chemicals used were purchased from Sigma-Aldrich and were used as received. 1,2-bis(decyloxy)benzene (**6**)[1] and 2,3-dibromo-6,7-bis(decyloxy)naphthalene (**8**)[2,3] were prepared according to literature procedures. Anhydrous and oxygen-free solvents were dispensed from a custom-built solvent purification system which used purification columns packed with activated alumina and supported copper catalyst (Glasscontour, Irvine, CA). Oven or flame-dried glassware was used for all reactions. Melting points were determined using a Barnstead Electrothermal 9100 melting point apparatus and are uncorrected. High resolution MALDI mass spectra were recorded at the Centre Régional de Spectrométrie de Masse à l'Université de Montréal using an Agilent LC-MSD TOF spectrometer.

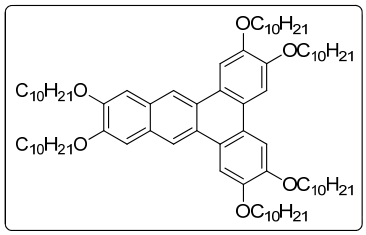


1-pinacolatoboron-3,4-bis(decyloxy)benzene (7).
200 mL cyclohexane was degassed with N_2 for 15 minutes. To the solvent, 4-4'-di-*tert*-butyl-2,2'-dipyridyl (0.102 g, 0.191 mmol), bis(pinacolato)diboron (5.42 g, 21.34 mmol) and $[Ir(OMe)COD]_2$ (0.191 g, 0.127 mmol) were added followed by 1,2-bis(decyloxy)benzene (7.45 g, 19.06 mmol). The solution was heated to 80°C and left to stir under N_2 for 2 days to and concentrated. The resulting oil was purified using column chromatography with hexanes/EtOAc (96:4) to give a colourless oil (7.74 g, 78.6 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, J = 8.1 Hz, 1H), 7.29 (s, 1H), 6.88 (d, J = 8.1 Hz, 1H), 4.05-3.99 (m, 4H), 1.84-1.79 (m, 4H), 1.33-1.24 (m, 40H), 0.90-0.88 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.20, 148.76, 128.85, 119.70, 112.96, 83.77, 69.48, 69.11, 32.15, 32.14, 29.87, 29.85, 29.82, 29.81, 29.68, 29.64, 29.59, 29.58, 29.43, 26.29, 26.23, 25.08, 22.92, 14.33.



2,3-bis[3,4-didecyloxyphenyl]-6,7-didecyloxynaphthalene (9).
$Pd(OAc)_2$ (0.037 g, 0.167 mmol) and PPh_3 (0.088 g, 0.334 mmol) were dissolved in 20 mL degassed toluene, followed by the addition of 2,3-dibromo-6,7-bis(decyloxy)naphthalene (2.00g, 3.34 mmol) and 1-pinacolatoboron-3,4-bis(decyloxy)benzene (3.61 g, 6.98 mmol). To the reaction mixture 7 mL degassed aq. 2.0 M K_3PO_4 (excess) was added. The mixture was heated to 80°C and left to stir for 48 hours. Solution cooled to room temperature, followed by the addition of 20 mL dichloromethane and washed with H_2O (2x20 mL) and brine (1x20 mL). The organic layer was dried with $MgSO_4$ and solvent removed under reduced pressure to give a light brown solid. The crude product was further purified using column chromatography with hexanes/dichloromethane (60:40) to yield a white solid (3.01 g, 74.0 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.68 (s, 2H), 7.14 (s, 2H), 6.79 (s, 4H), 6.66 (s, 2H), 4.12 (t, J = 6.6 Hz, 4H), 3.96 (t, J = 6.6 Hz, 4H), 3.70 (t, J = 6.6 Hz, 4H), 1.93-1.89 (m, 4H), 1.83-1.79 (m, 4H), 1.70-1.65 (m, 4H), 1.46-1.28 (m, 84H), 0.91-0.87 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 150.00, 148.60, 148.01, 137.23, 135.11, 128.69, 127.69, 122.29, 116.52, 113.63, 107.83, 69.55, 69.35, 69.14, 32.20, 32.18, 29.98, 29.92, 29.90, 29.88, 29.85, 29.77, 29.72, 29.71, 29.66, 29.63, 29.62, 29.42,

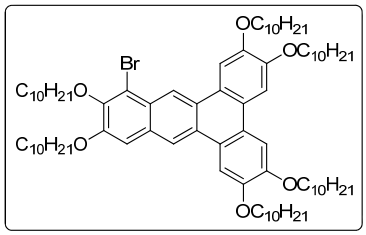
29.38, 26.35, 26.31, 22.95, 14.35. HRMS (MALDI) calc'd for $C_{82}H_{136}O_6$+H *m/z* 1217.0337, found 1217.0331.



2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (3).

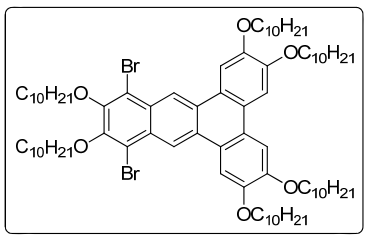
2,3-bis[3,4-didecyloxyphenyl]-6,7-didecyloxynaphthalene (1.214g, 1.00 mmol) was dissolved in 20 mL dry CH_2Cl_2. $FeCl_3$ (0.97 g, 6.00 mmol) was added to the solution and stirred for 1 hour. The solution was poured into MeOH (100 mL) and the resulting precipitate was collected by suction filtration. The crude product was purified by a short silica column eluting with CH_2Cl_2 and the solvent was removed via rotary evaporator, followed by recrystallization in acetone to yield a light yellow solid (1.11 g, 91.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (s, 2H), 8.10 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.28-4.20 (m, 12H), 1.97-1.95 (m, 12H), 1.59-1.55 (m, 12H), 1.43-1.28 (m, 72H), 0.91-0.87 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 150.08, 149.50, 149.28, 128.31, 126.71, 124.29, 124.16, 119.55, 107.96, 107.74, 107.04, 70.03, 69.65, 69.07, 32.17, 29.94, 29.91, 29.87, 29.85, 29.79, 29.77, 29.72, 29.63, 29.39, 26.45, 26.39, 22.94, 14.35. HRMS (MALDI) calc'd for $C_{82}H_{134}O_6$+H *m/z* 1215.0180, found 1215.0175.

Synthesis of 10-bromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (4a).



2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene, (0.250 g, 0.206 mmol) was dissolved in 50 mL $CHCl_3$. Bromine (0.035 g, 0.216 mmol) was added dropwise to the solution and left to stir for 1 hour. The organic layer was washed with sodium thiosulfate, water then brine. The organic layer was dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. A column was performed on the crude product using hexanes/DCM (50:50), followed by recrystallization in acetone to yield a pale yellow/brown solid (0.243 g, 91.1 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 30 mM): δ 9.15 (s, 1H), 8.65 (s, 1H), 8.17 (s, 1H), 8.07 (s, 1H), 7.78 (s, 2H), 7.30 (s, 1H), 4.31-4.22 (m, 8H), 4.18-4.16 (m, 4H), 1.98-1.91 (m, 12H), 1.60-1.56 (m, 12H), 1.42-1.29 (m, 84H), 0.91-0.87 (m, 18H). ^{13}C-NMR (300 MHz, $CDCl_3$): *δ* 152.29, 149.98, 149.87, 149.36, 149.26, 147.17, 129.89, 128.14, 127.36, 126.51, 124.73, 124.30, 124.16, 123.48, 120.69, 119.96, 116.28, 108.15, 107.96, 107.81, 107.70, 106.84, 73.94, 69.99, 69.92, 69.69, 68.93, 32.18, 30.63, 29.96, 29.92, 29.89, 29.81, 29.74, 29.64, 29.53, 26.53, 26.46, 22.95, 14.36. HRMS (MALDI) calc'd for $C_{82}H_{133}BrO_6$+H *m/z* 1292.9286, found 1292.9280.

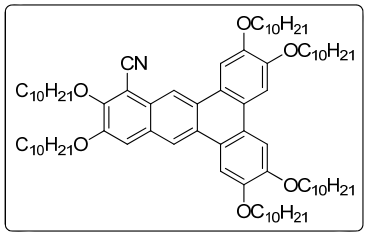
Synthesis of 10,13-dibromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (5a).



2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.300 g, 0.247 mmol) was dissolved in 50 mL chloroform. Br_2 (0.029 mL, 0.567 mmol) was added dropwise to the solution and the mixture was left to stir for 1 hour. The reaction was washed with saturated sodium thiosulfate (50 mL), water (50 mL) then brine (50 mL). The organic layer was dried with $MgSO_4$, filtered then dried. The crude product was purified using column chromatography using exanes/dichloromethane (60:40). The product was then recrystallized in acetone to yield a light brown solid (0.319 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (s, 2H), 8.18 (s, 2H), 7.79 (s,

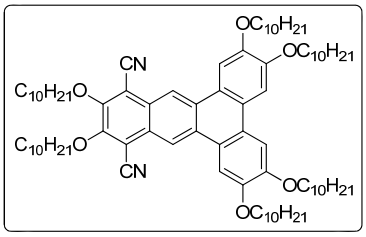
2H), 4.32 (t, *J* = 6.60 4H), 4.43 (t, *J* = 6.30), 4.18 (t, *J* = 6.30, 4H), 2.00-1.91 (m, 12H), 1.60-1.54 (m, 12H), 1.38-1.26 (m, 72H), 0.90-0.86 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 150.47, 150.02, 149.43, 129.04, 128.14, 124.98, 123.39, 121.29, 116.20, 108.34, 107.67, 74.83, 69.94, 69.80, 32.17, 30.59, 29.95, 29.93, 29.91, 29.87, 29.78, 29.62, 29.60, 26.43, 26.39, 25.00, 22.94, 14.34. HRMS (MALDI) calc'd for $C_{82}H_{132}Br_2O_6$+H *m/z* 1370.8391, found 1370.8385.

Synthesis of 10-cyano-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (4b).



10-bromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.10 g, 0.077 mmol) was dissolved in dry DMF (5 mL). CuCN (9.0 mg, 0.10 mmol) was added to the solution. Reaction was fitted with a condenser and heated to reflux for 18 hours under N_2. The solution was cooled to room temperature, followed by the addition of 20 mL of water. Ethylenediamine (1 mL) was added to the solution and shaken. The mixture was extracted with DCM (3 x 25 mL), and the combined extracts were washed with water followed by 1 M HCl. The organic layer was dried with $MgSO_4$, filtered and solvent removed under reduced pressure. A brown solid crude product was obtained. Column chromatography was performed using hexanes/dichloromethane (50:50), followed by recrystallization in acetone to yield a bright yellow solid (0.042 g, 48 %). ^{1}H-NMR (300 MHz, $CDCl_3$) : δ 8.73 (s, 1H), 8.37 (s, 1H), 7.94 (s, 1H), 7.80 (s, 1H), 7.63 (s, 1H), 7.62 (s, 1H), 7.28 (s, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 4.30-4.22 (m, 8H), 4.17 (t, *J* = 6.3 Hz, 2H), 1.96-1.91 (m, 12H), 1.56-1.52 (m, 12H), 1.43-1.26 (m, 72H), 0.93-0.89 (m, 18H). ^{13}C-NMR (300 MHz, $CDCl_3$): *δ*154.90, 150.62, 150.08, 150.00, 149.44, 149.14, 128.38, 128.35, 128.13, 125.76, 124.57, 124.37, 123.40, 123.04, 120.10, 117.59, 116.11, 112.17, 107.66, 107.52, 107.45, 107.28, 101.80, 75.36, 69.89, 69.72, 69.58, 69.10, 32.21, 32.20, 30.61, 30.01, 29.99, 29.93, 29.89, 29.80, 29.76, 29.68, 29.65, 29.48, 26.52, 26.19, 22.97, 14.37. HRMS (MALDI) calc'd for $C_{83}H_{133}NO_6$+H *m/z* 1240.0133, found 1240.0127.

Synthesis of 10,13-dicyano-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (5b).



10,13-dibromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.42 g, 0.306 mmol) was dissolved in 10 mL dry DMF. CuCN (69 mg, 0.76 mmol) was added to the solution. Reaction was heated to reflux and stirred for 24 hours under N_2. The solution was then cooled to room temperature; 10 mL of ethylenediamine was added, followed by 20 mL H_2O. It was then extracted with DCM (3x20 mL). The organic layer was washed with 1 M HCl (3x50 mL), H_2O (50 mL) and brine (50 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography was performed with hexanes/dichloromethane (60:40), followed by recrystallization in acetone to yield a bright orange solid (0.04 g, 10.3%). ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* 8.63 (s, 2H), 7.71 (s, 2H), 7.58 (s, 2H), 4.44 (t, *J* = 6.9 Hz, 4H), 4.21 (m, 8H), 1.96 (m, 12H), 1.61 (m, 12H), 1.29 (m, 72H), 0.89 (m, 18H). ^{13}C-NMR (300 MHz, $CDCl_3$): *δ* 155.71, 150.55, 149.14, 129.72, 126.17, 124.72, 122.01, 118.29, 114.95, 107.02, 106.72, 106.50, 76.31, 69.50, 69.30, 32.19, 30.57, 30.04, 30.00, 29.97, 29.96, 29.94, 29.78, 29.75, 29.72, 29.66, 29.64, 26.50, 26.18, 22.94, 14.35. HRMS (MALDI) calc'd for $C_{83}H_{133}NO_6$+H *m/z* 1265.0085, found 1265.0080.

Mesophase Characterization

Polarized optical microscopy studies were carried out using an Olympus BX-51 polarized optical microscope equipped with a Linkam LTS 350 heating stage and a digital camera. Differential Scanning Calorimetry (DSC) studies were carried out using a TA Instruments DSC Q200 with a scanning rate of 5 °C/min. Variable temperature X-Ray diffraction measurements were carried out on a Rigaku RAXIS rapid diffractometer using Cu Kα radiation (λ=1.5418Å), a graphite monochromator and a Fujifilm Co. Ltd curved image plate (460 mm x 256 mm). Samples were heated to the isotropic liquid phase on a hot plate and loaded by capillary action. Excess material was cleaned off the sides with clean dry tweezers. Capillaries were then cut to length and mounted in our capillary furnace. Temperature was controlled with an Omega temperature controller connected to the capillary furnace with a K-type thermocouple for feedback. Owing to technical issues, the controller was set to manual mode. Due to thermal equilibration, the temperature often dropped during a run. Only the final temperature is reported. A 0.3 mm collimator was used and all samples were irradiated for 30 minutes. Peaks and their respective angle measurements and d-spacings were determined using the MDL JADE software. Peak type was analyzed by taking the reciprocal d-spacings and dividing them by the highest intensity peak. Only peaks with greater than 1% intensity in the low angle region were reported in this précis. Columnar hexagonal unit cell parameters were determined from the d-spacing using the formula $a = \frac{2}{\sqrt{3}} d$ which is derived from the sine relationship in right angle triangles formed by inscribing the hexagonal unit cell in a rectangle.

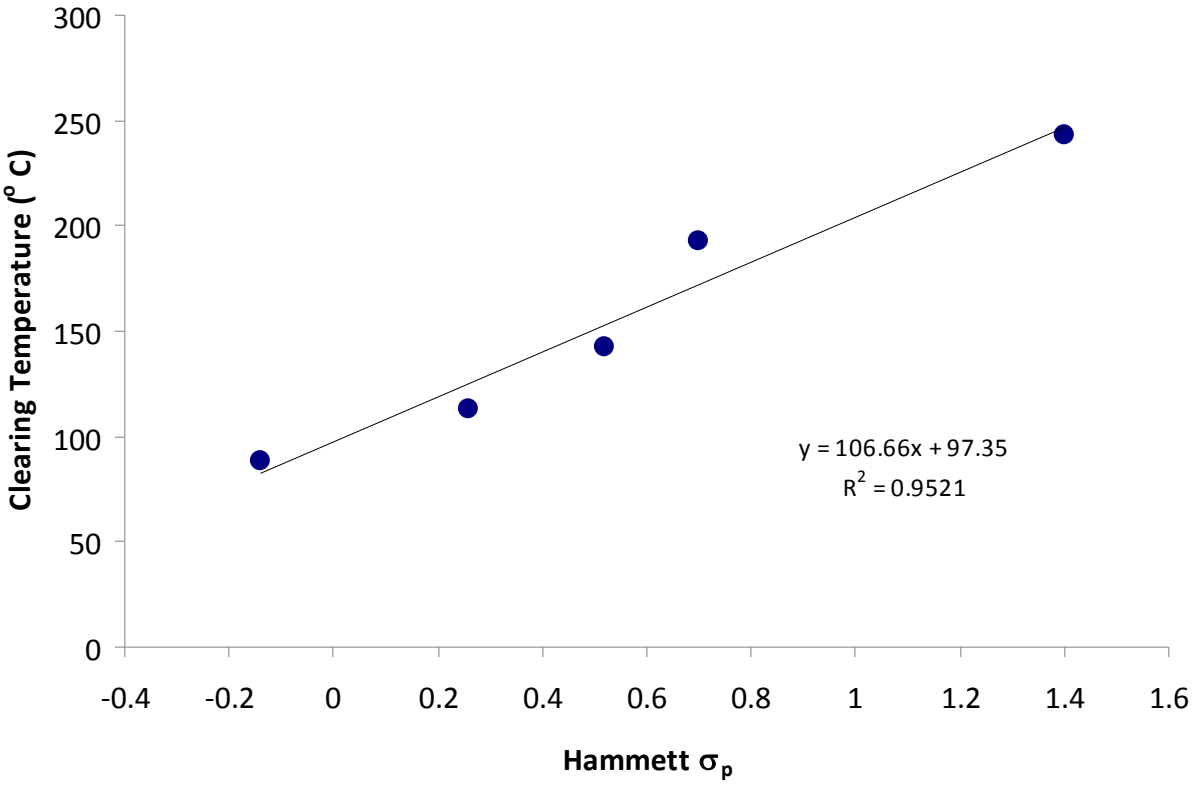


Figure S1. Plot of clearing temperature as a function of Hammett σ_p values for compounds **2**,[4] **4a**, **4b**, **5a**, and **5b**. Compound **3** was not included because it does not exhibit a liquid crystalline phase. For the disubstituted compounds (**5a** and **5b**), the sum of the σ_p values for the two substituents were used.

References

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3. P. T. Lynett, K. E. Maly, *Org. Lett.* 2009, **11**, 3726-3729.

4. K. Lau, J. Foster, and V. Williams, Chem. Commun. 2003, 2172-2173.

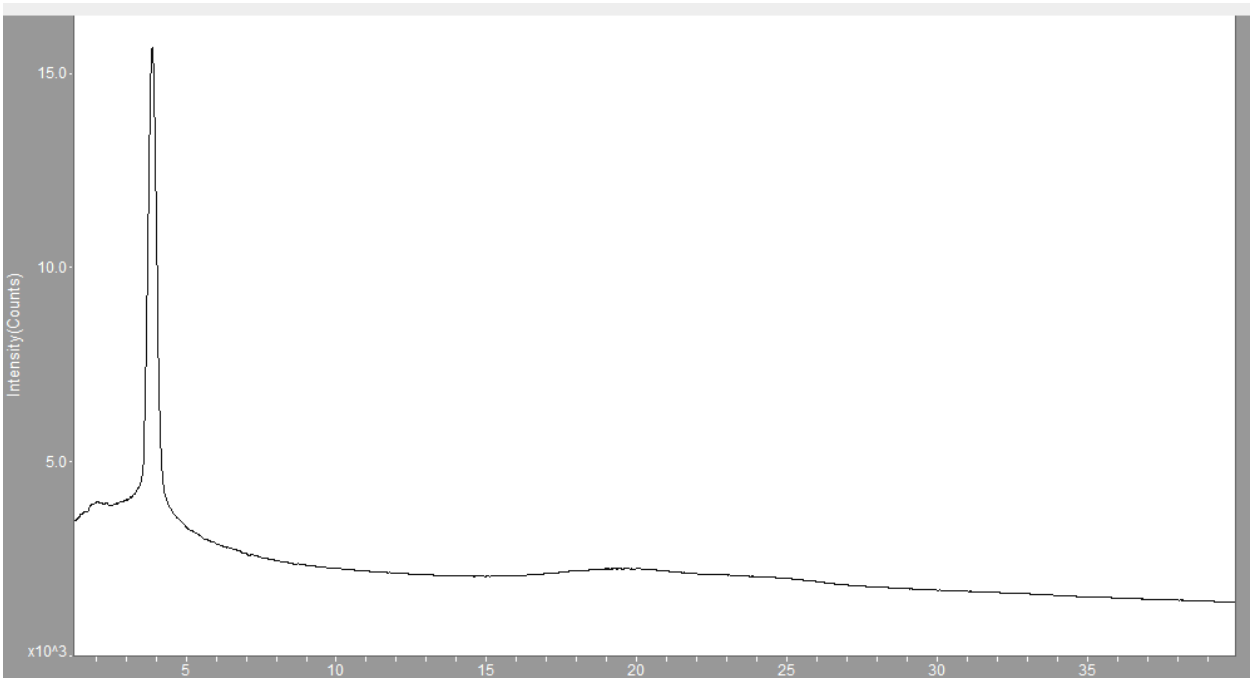


Figure S2. Representative XRD data for **4a** (Intensity vs. 2θ).

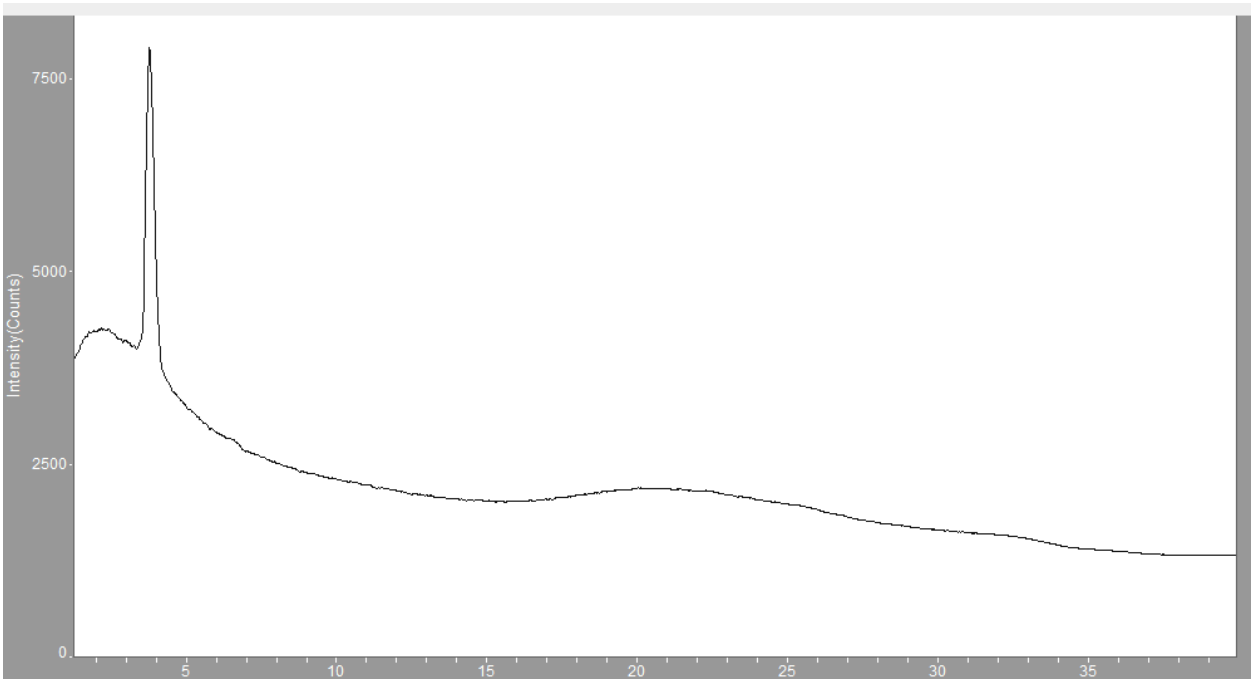


Figure S3. Representative XRD data for **4a** (Intensity vs. 2θ).

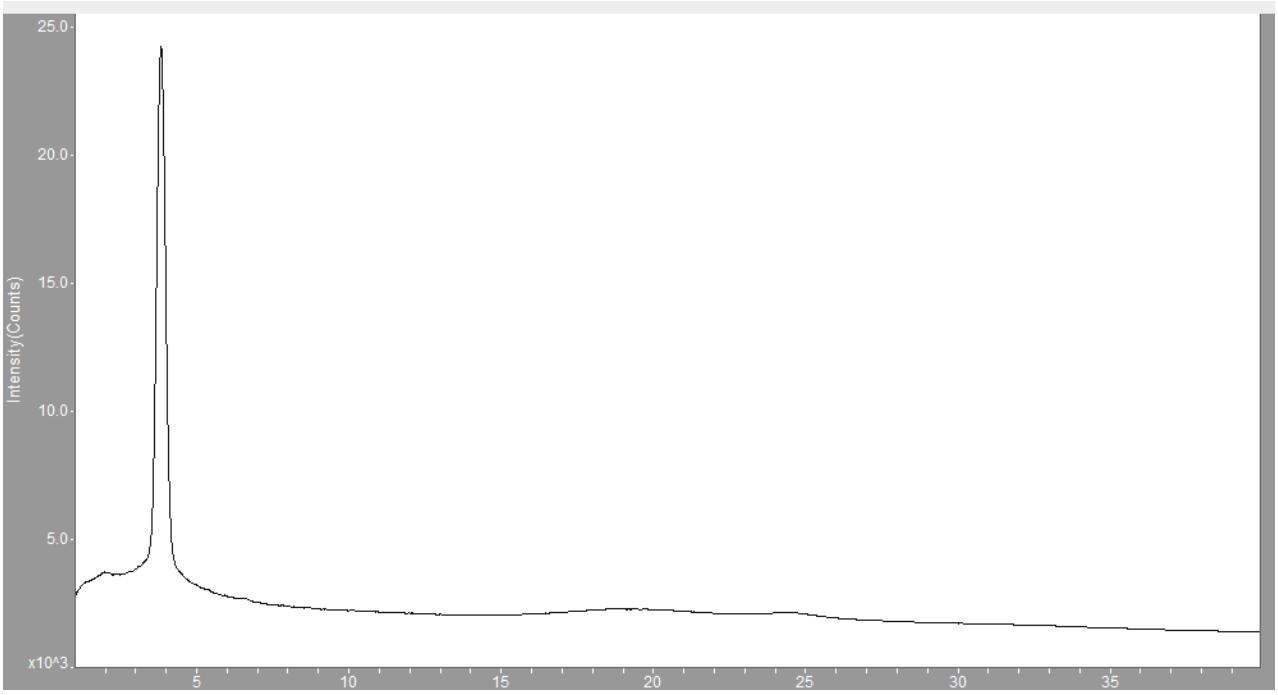


Figure S4. Representative XRD data for **5a** (Intensity vs. 2θ).

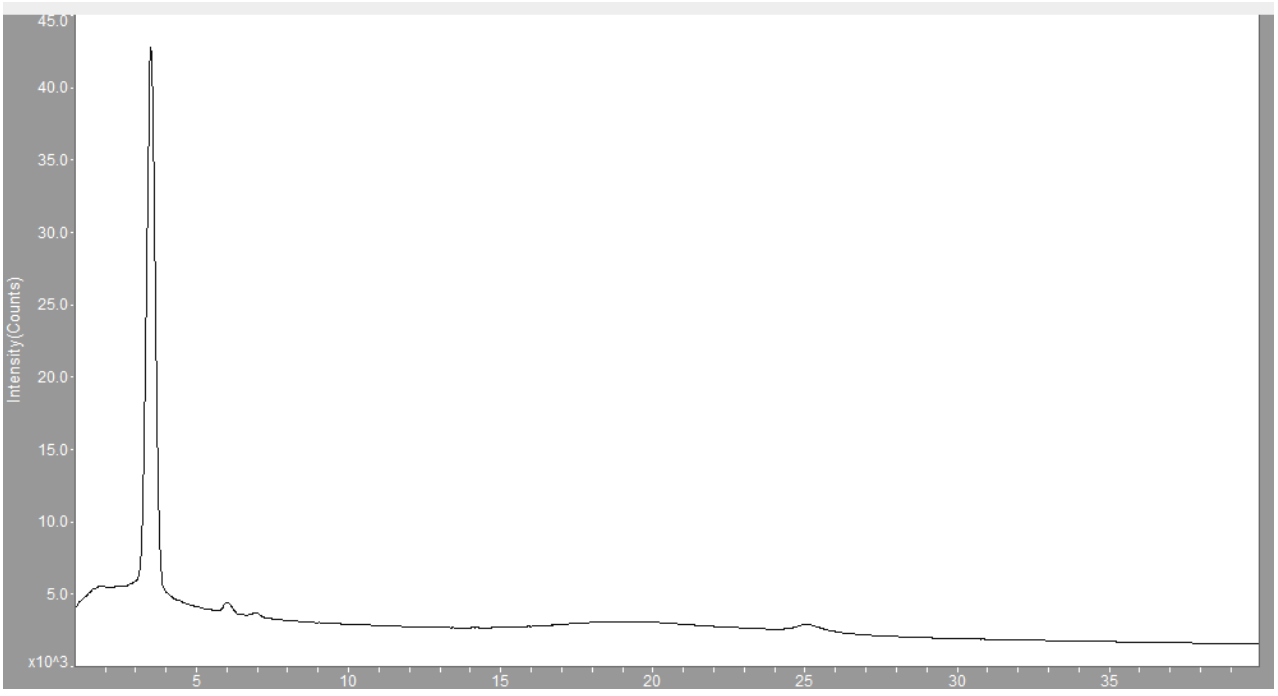
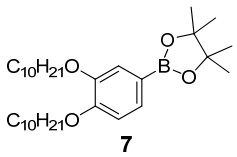


Figure S5. Representative XRD data for **5a** (Intensity vs. 2θ).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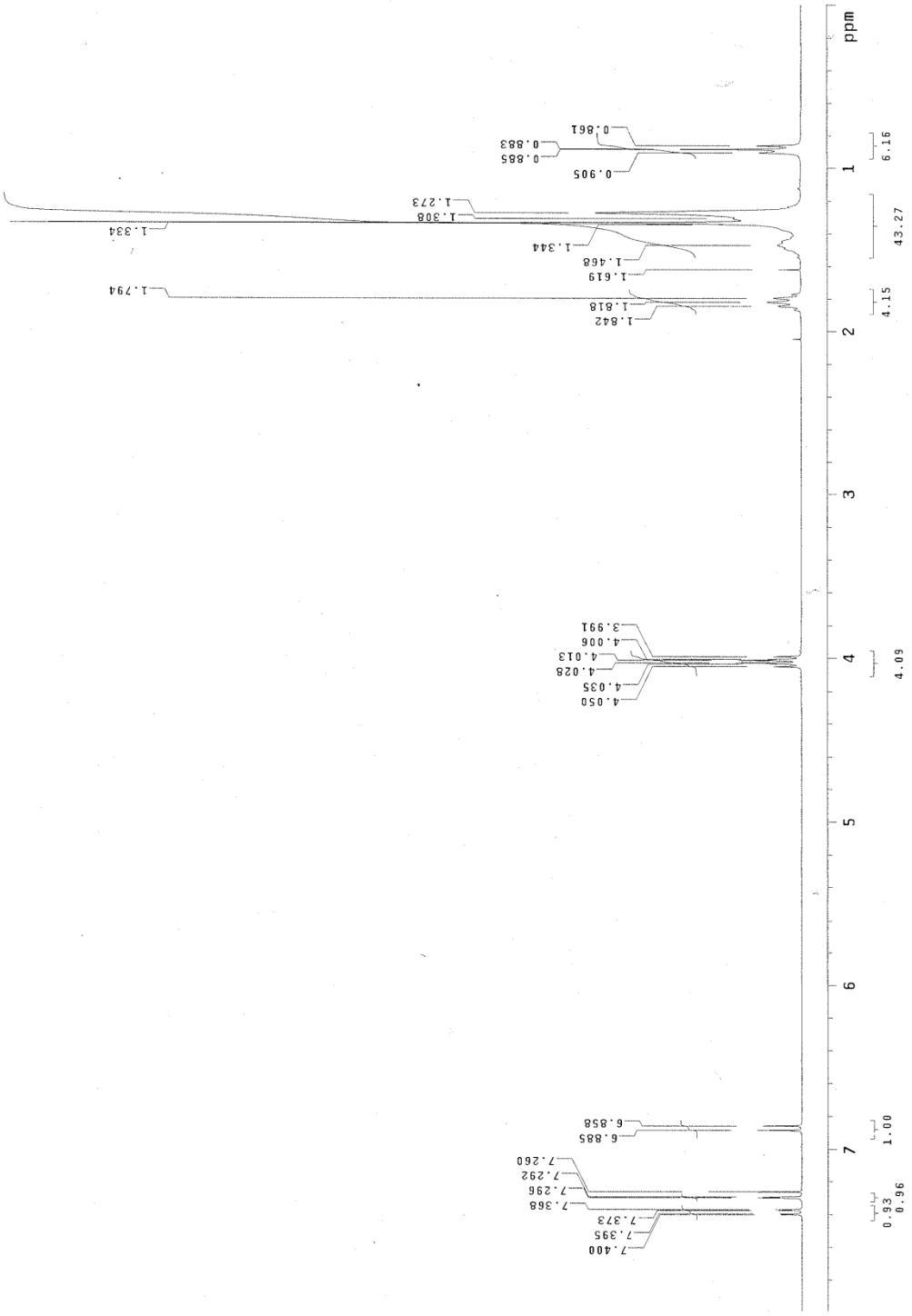
B
O

7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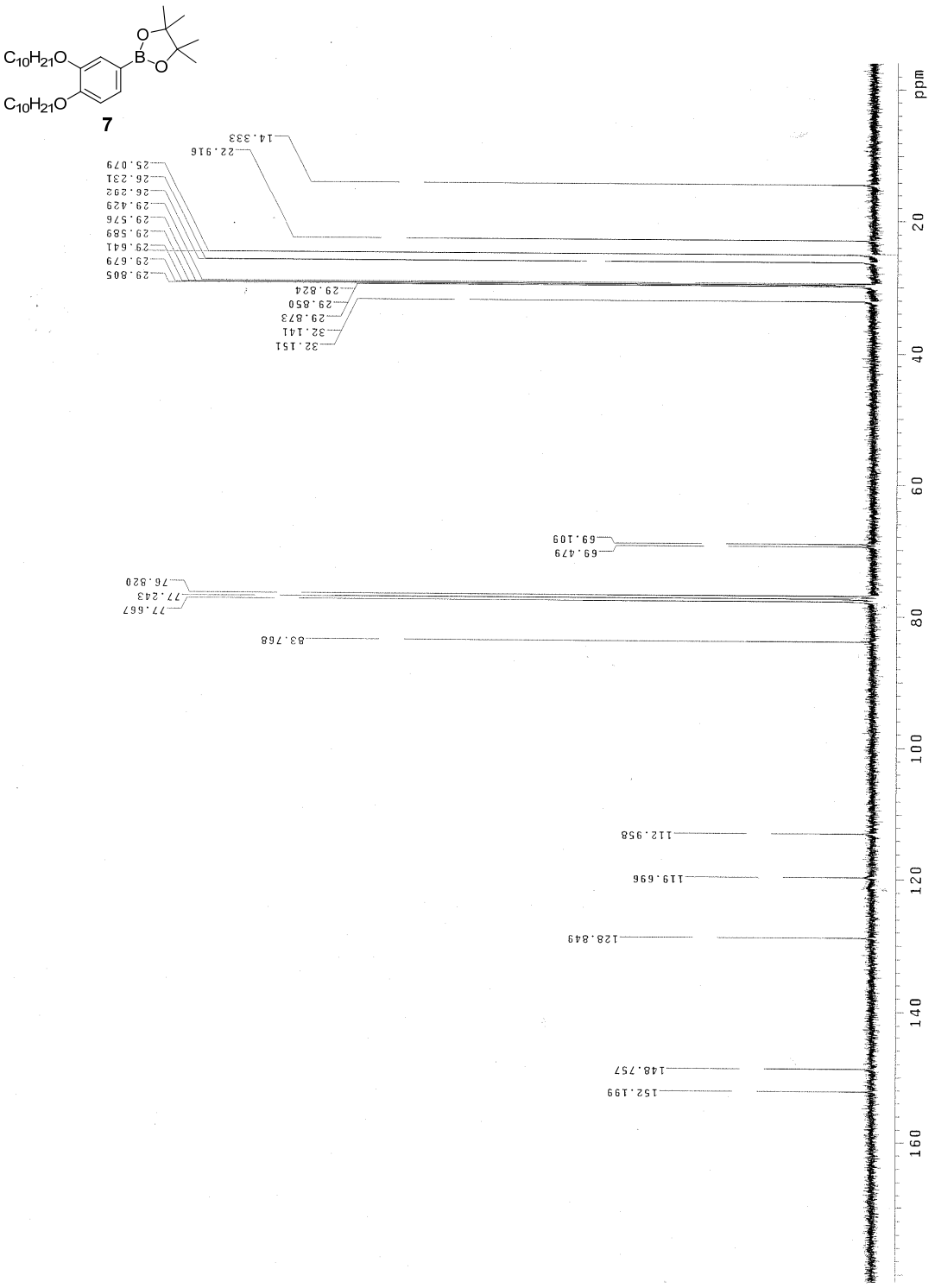
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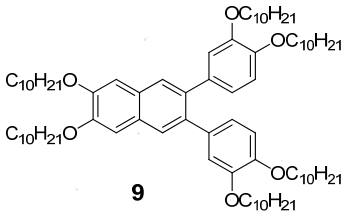

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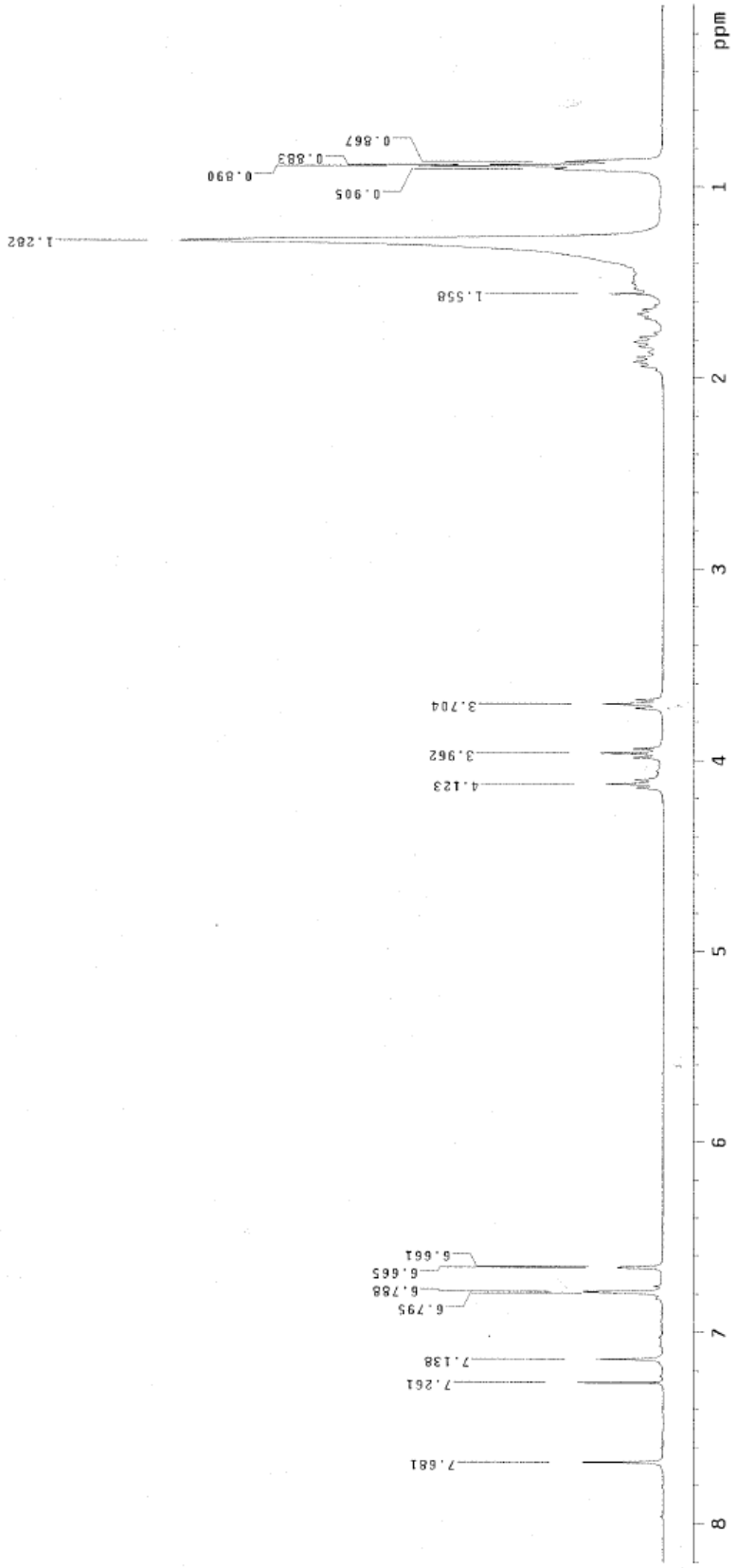

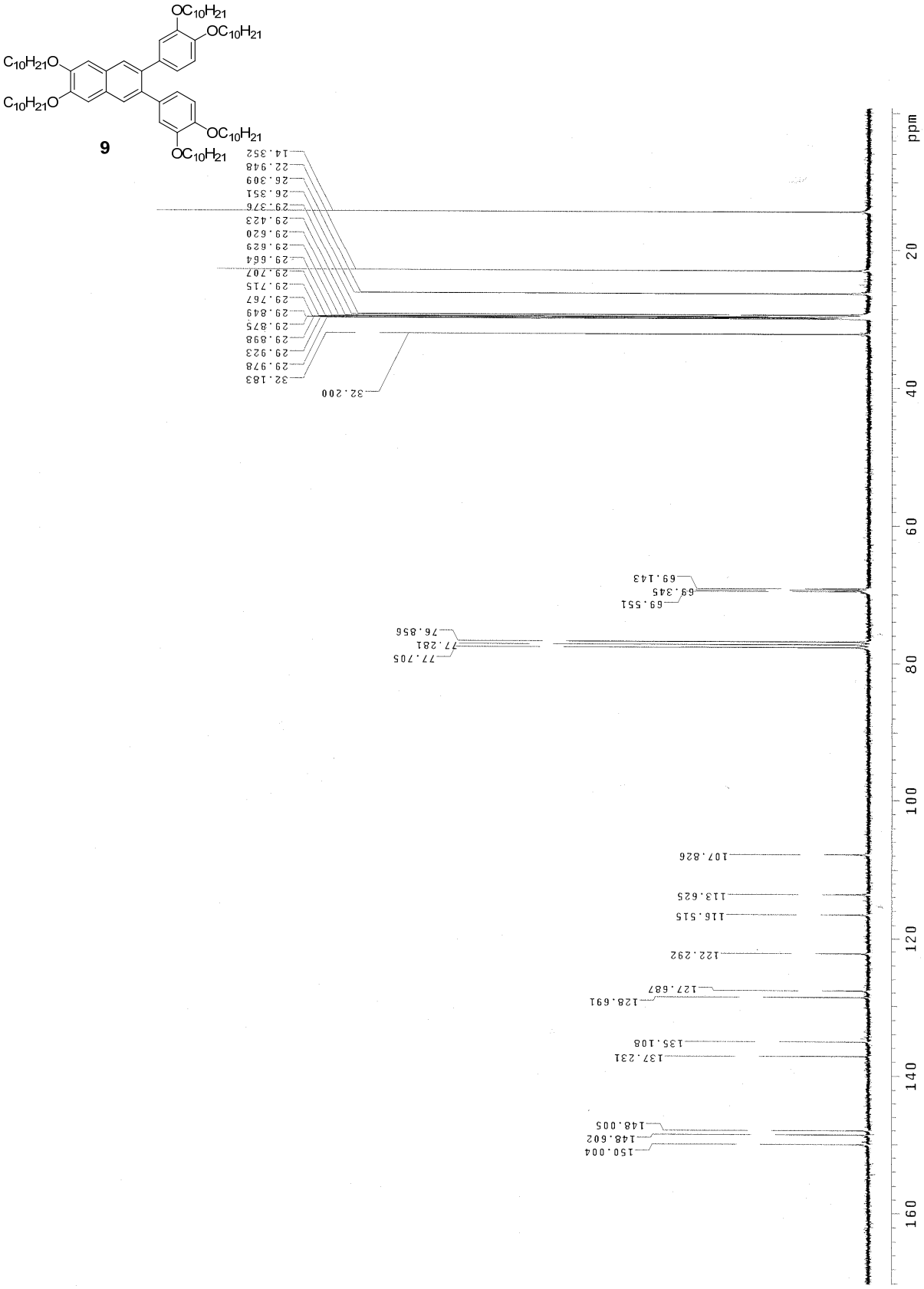
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107.826
113.625
116.515
122.292
127.687
128.691
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148.602
150.004
ppm
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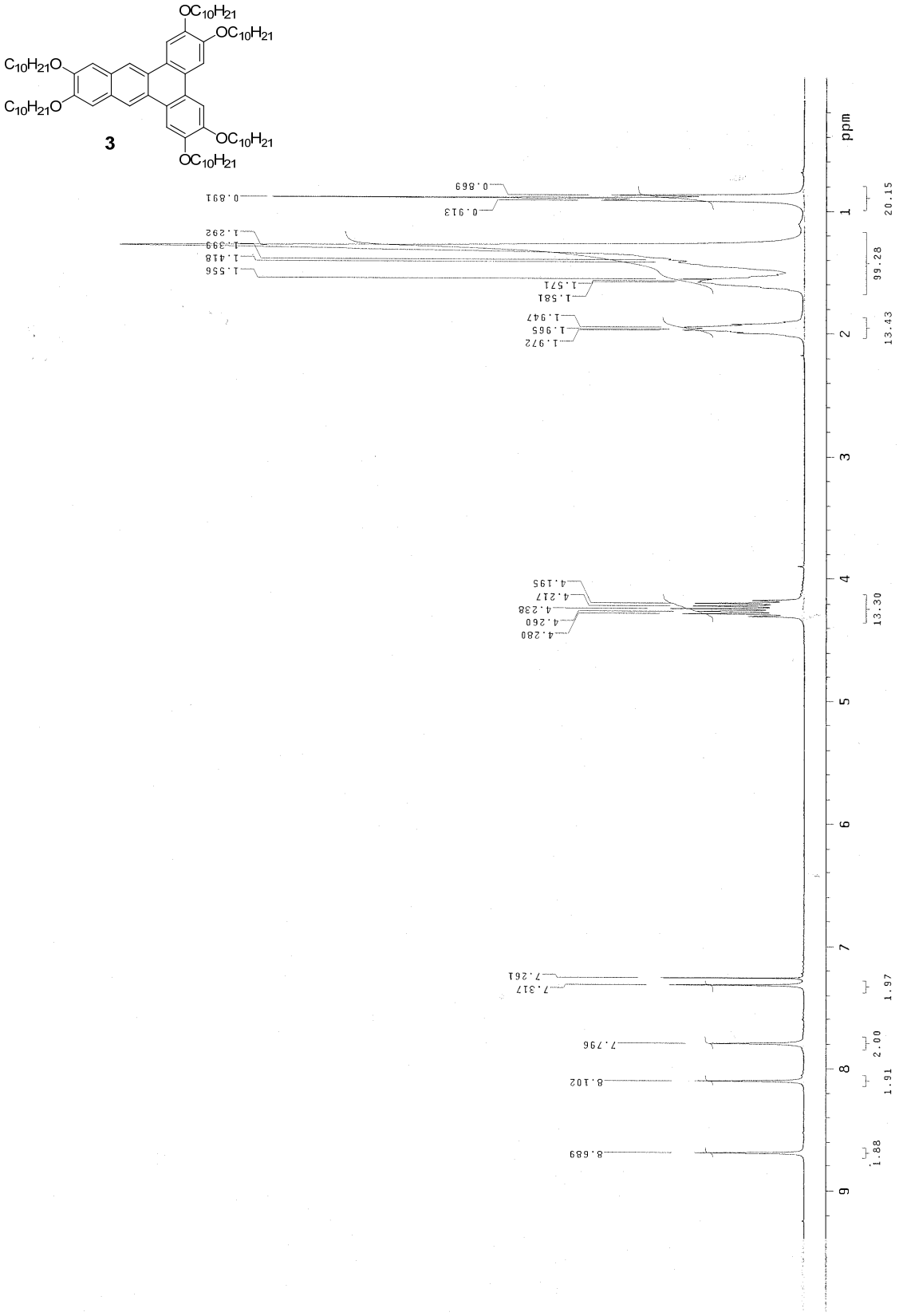
40
60
80
100
120
140
160


OC10H21
OC10H21
C10H21O
C10H21O
OC10H21
OC10H21
3
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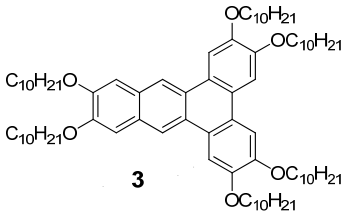
0.891
0.913
1.292
1.399
1.418
1.556
1.571
1.581
1.947
1.965
1.972
4.195
4.217
4.238
4.260
4.280
7.261
7.317
7.796
8.102
8.689
ppm
1
2
3
4
5
6
7
8
9
20.15
99.28
13.43
13.30
1.97
2.00
1.91
1.88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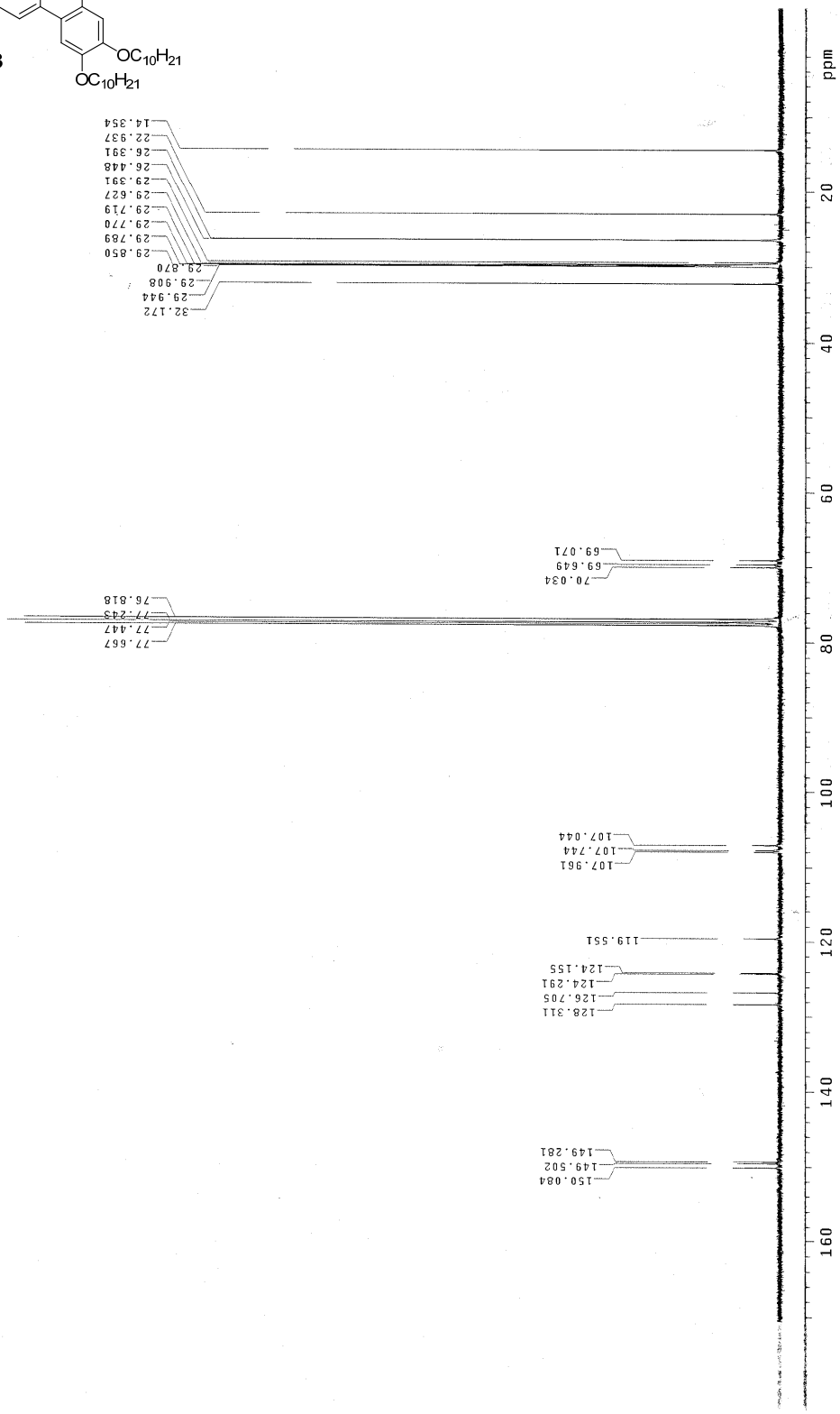
OC10H21
C10H21O
C10H21O
OC10H21
OC10H21

3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22.937
26.391
26.448
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29.627
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29.770
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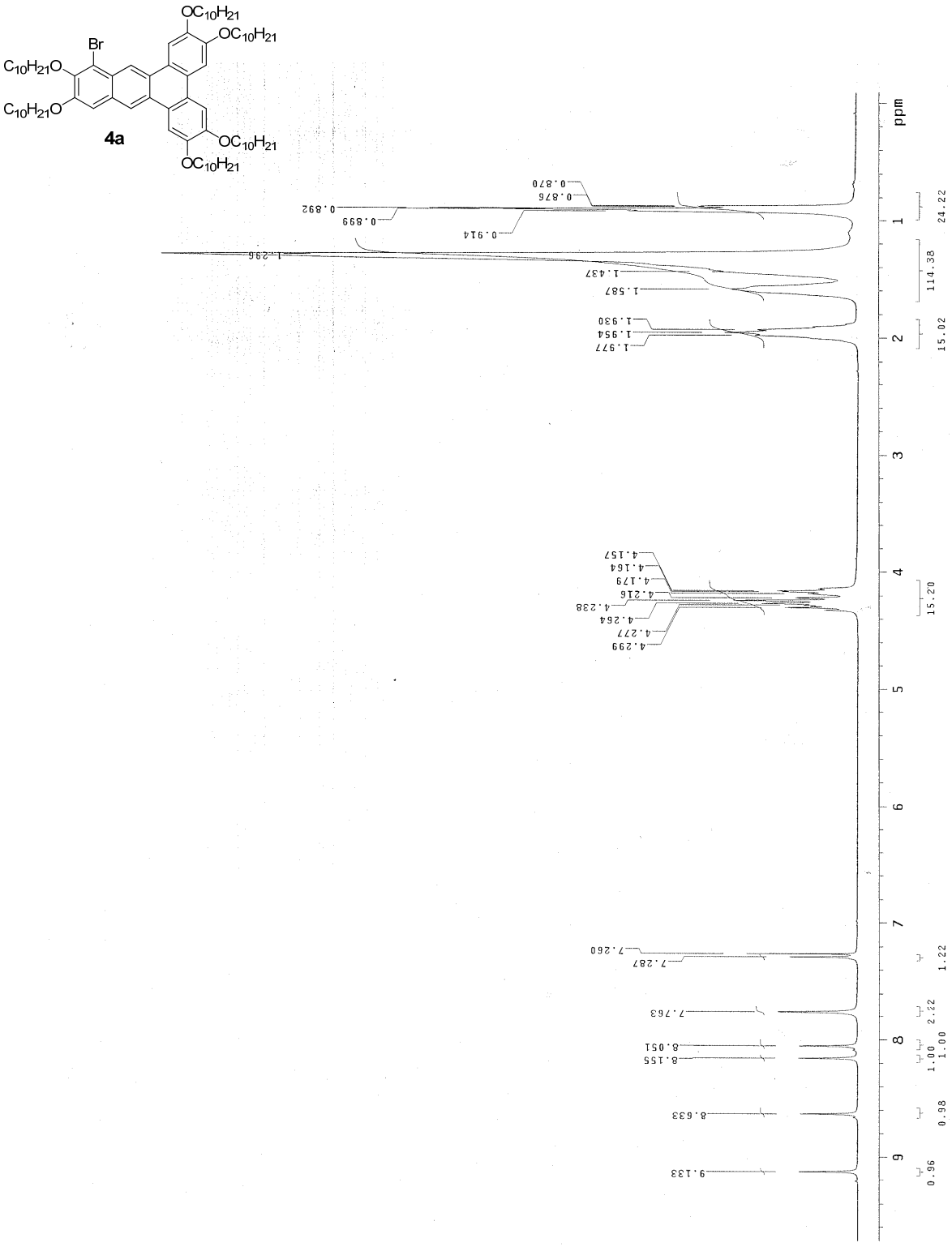
29.850
29.870
29.908
29.944
32.172
69.071
69.649
70.034
76.818
77.243
77.447
77.667
107.044
107.744
107.961
119.551
124.155
124.291
126.705
128.311
149.281
149.502
150.084
ppm
20
40
60
80
100
120
140
160


OC10H21
OC10H21
Br
C10H21O
C10H21O
OC10H21
OC10H21
4a
0.870
0.876
0.892
0.899
0.914
1.296
1.437
1.587
1.930
1.954
1.977
4.157
4.164
4.179
4.216
4.238
4.264
4.277
4.299
7.260
7.287
7.763
8.051
8.155
8.633
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ppm
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114.38
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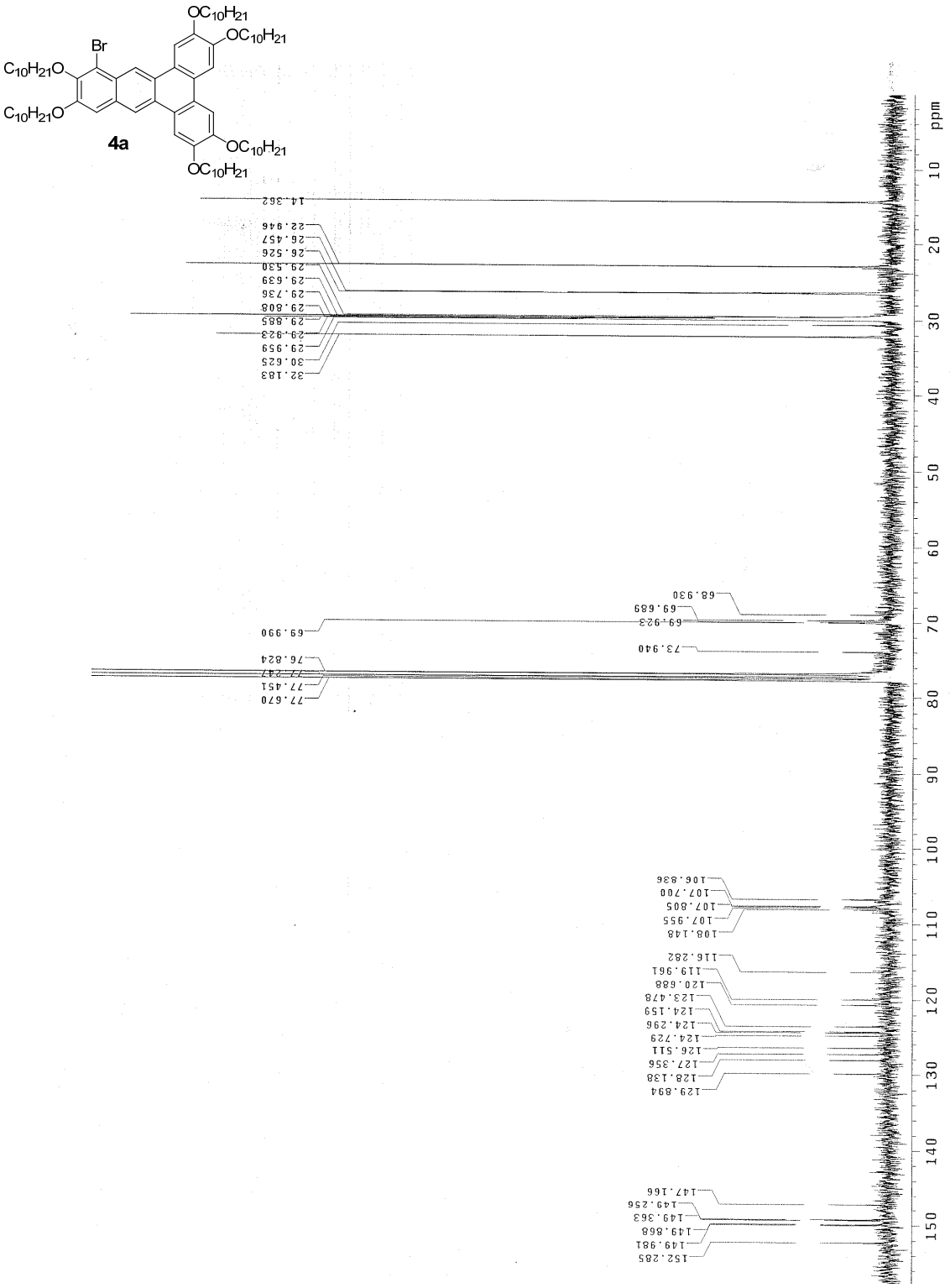
15.20
1.22
2.22
1.00
1.00
0.98
0.96


OC10H21
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Br
C10H21O
C10H21O
4a
OC10H21
OC10H21
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26.457
26.526
29.530
29.639
29.736
29.808
29.865
29.923
29.959
30.625
32.183
68.930
69.689
69.923
69.990
73.940
76.824
77.247
77.451
77.670
106.836
107.700
107.805
107.955
108.148
116.282
119.961
120.688
123.478
124.159
124.296
124.729
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127.356
128.138
129.894
147.166
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149.363
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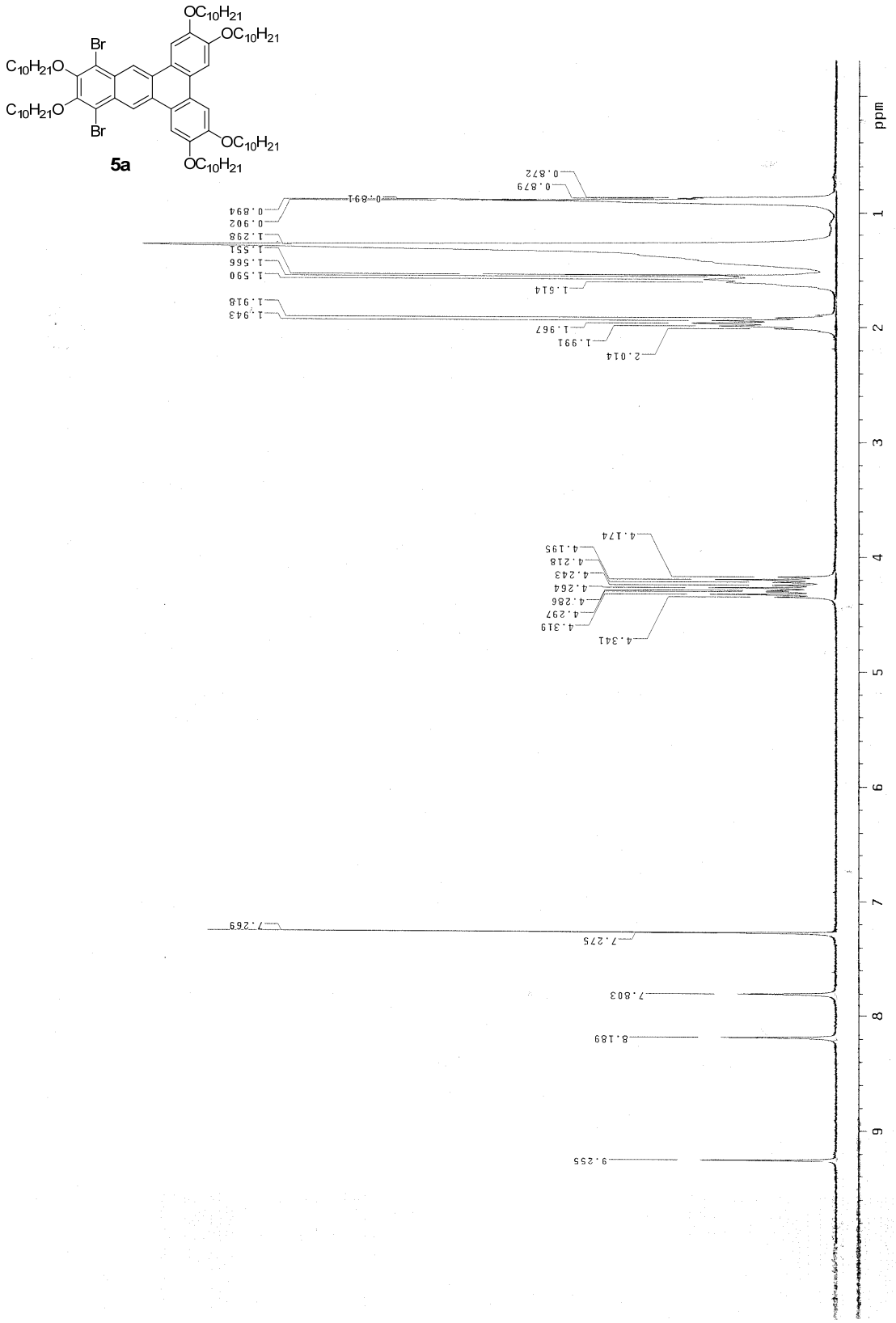
152.285
ppm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OC10H21
Br
C10H21O
C10H21O
Br
OC10H21
OC10H21
5a
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0.879
0.891
0.894
0.902
1.298
1.551
1.566
1.590
1.614
1.918
1.943
1.967
1.991
2.014
4.174
4.195
4.218
4.243
4.264
4.286
4.297
4.319
4.341
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7.275
7.803
8.189
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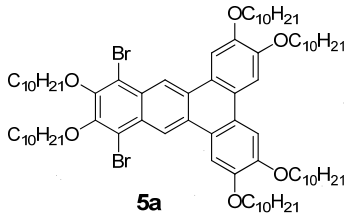
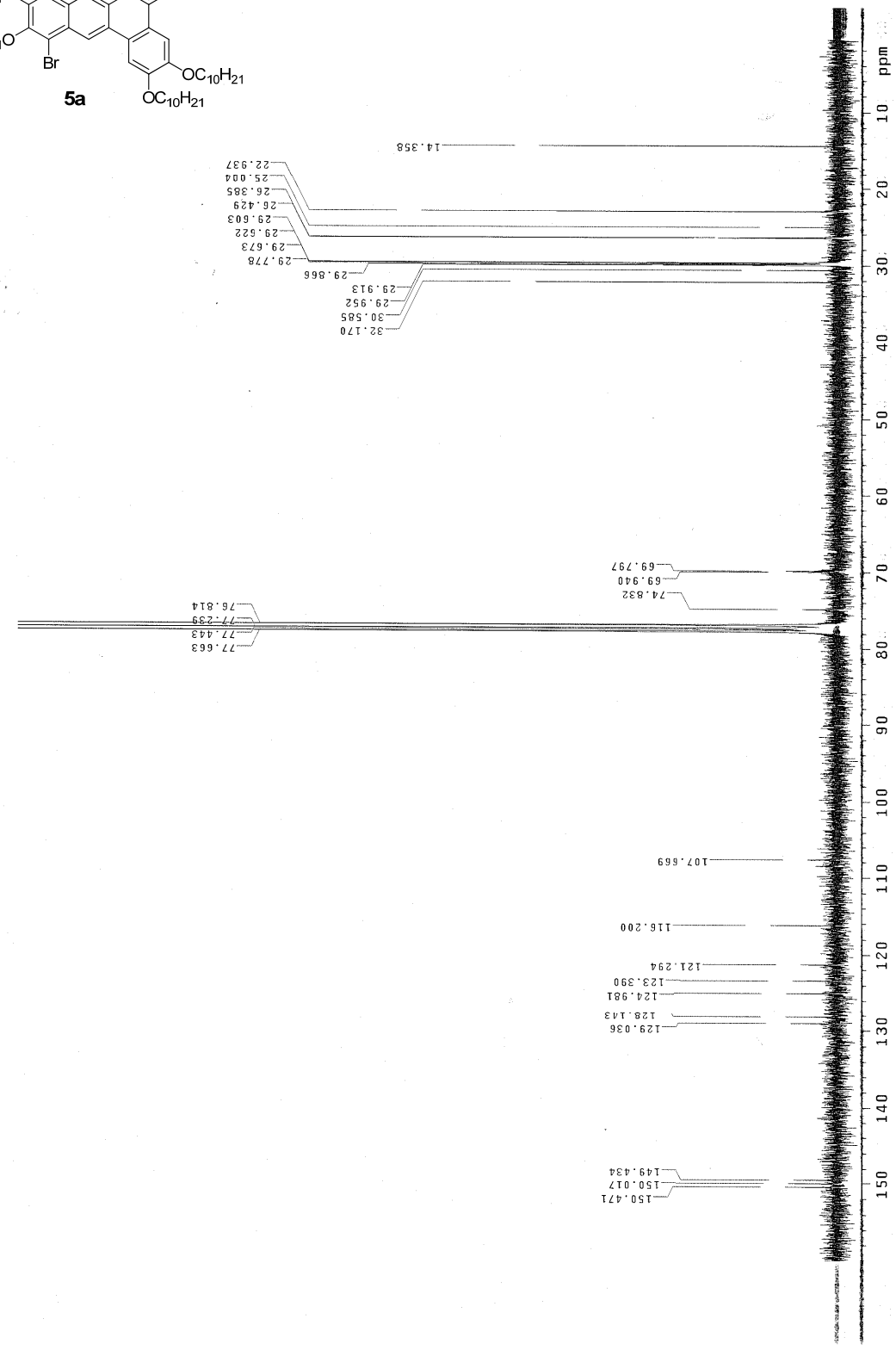
ppm


OC10H21
OC10H21
Br
C10H21O
C10H21O
Br
OC10H21
OC10H21

5a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29.622
29.673
29.778
29.866
29.913
29.952
30.585
32.170
69.797
69.940
74.832
76.814
77.239
77.443
77.663
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116.200
121.294
123.390
124.981
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129.036
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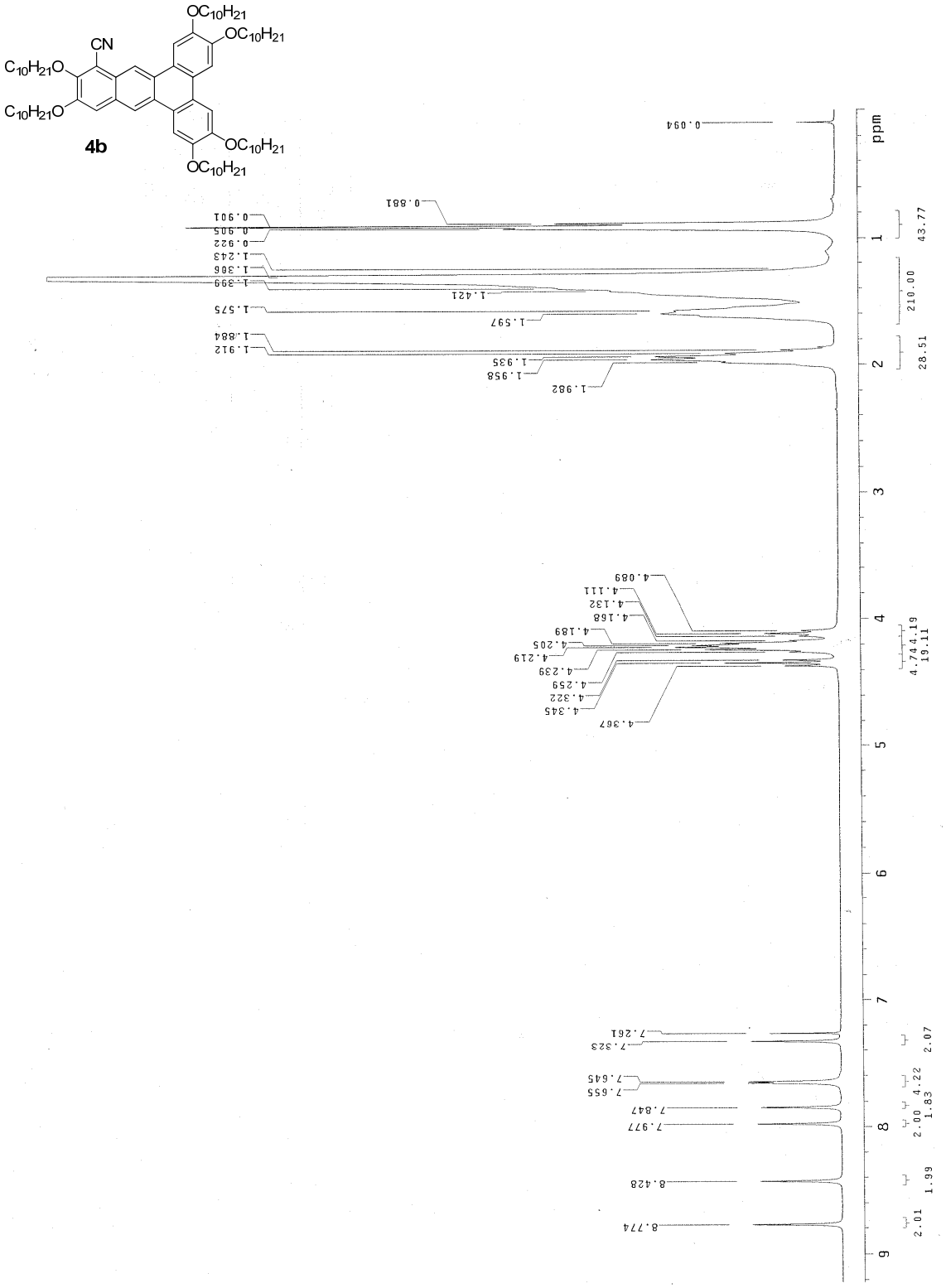
ppm


OC10H21
OC10H21
CN
C10H21O
C10H21O
OC10H21
OC10H21
4b
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0.861
0.901
0.905
0.922
1.243
1.306
1.399
1.421
1.575
1.597
1.884
1.912
1.935
1.958
1.982
4.089
4.111
4.132
4.168
4.189
4.205
4.219
4.239
4.259
4.322
4.345
4.367
7.261
7.323
7.645
7.655
7.847
7.977
8.428
8.774
ppm
1
2
3
4
5
6
7
8
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43.77
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4.74
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19.11
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4.22
2.00
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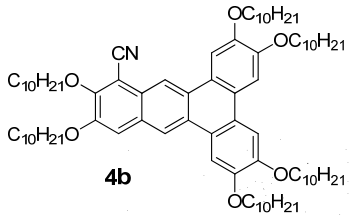
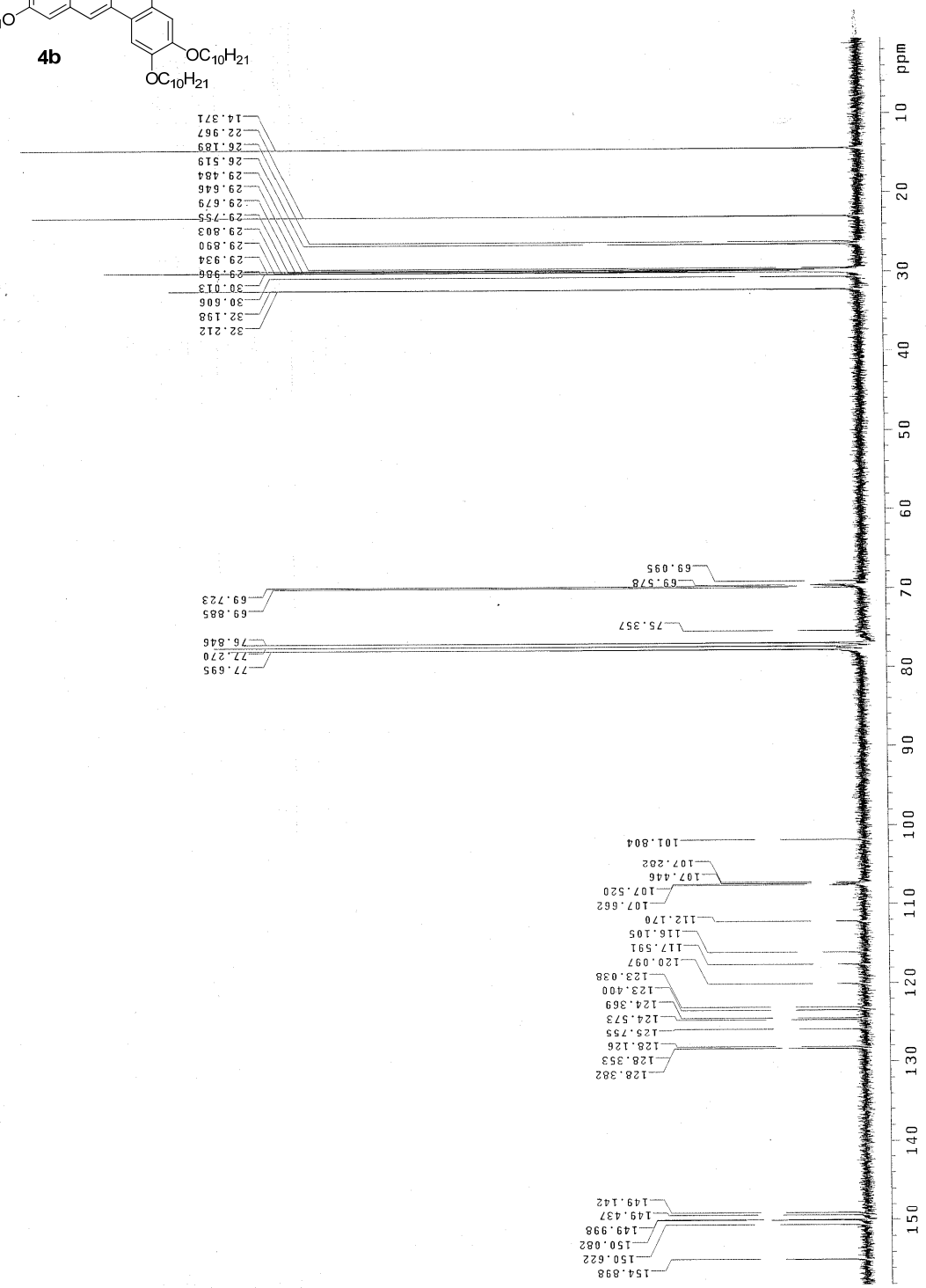
1.99
2.01


OC10H21
OC10H21
CN
C10H21O
C10H21O
OC10H21
OC10H21

4b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29.934
29.966
30.013
30.606
32.198
32.212
69.095
69.578
69.723
69.885
75.357
76.846
77.270
77.695
101.804
107.262
107.446
107.520
107.662
112.170
116.105
117.591
120.097
123.038
123.400
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124.573
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128.126
128.353
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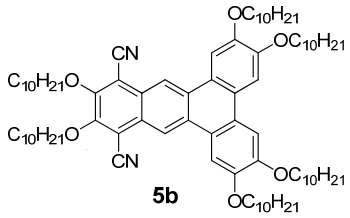
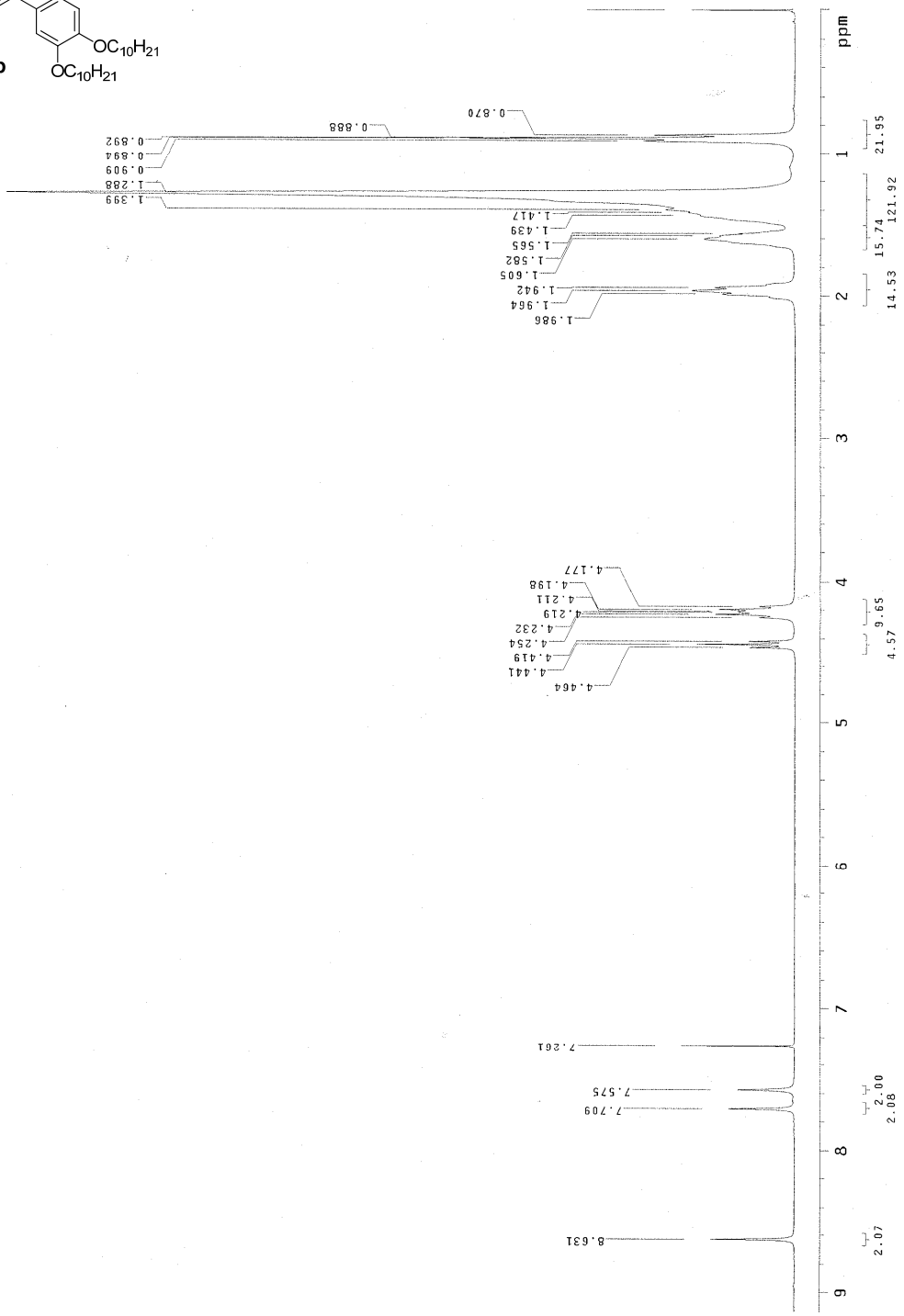
154.898
ppm


OC10H21
OC10H21
CN
C10H21O
C10H21O
CN
OC10H21
OC10H21

5b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0.888
0.892
0.894
0.909
1.288
1.399
1.417
1.439
1.565
1.582
1.605
1.942
1.964
1.986
4.177
4.198
4.211
4.219
4.232
4.254
4.419
4.441
4.464
7.261
7.575
7.709
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ppm
21.95
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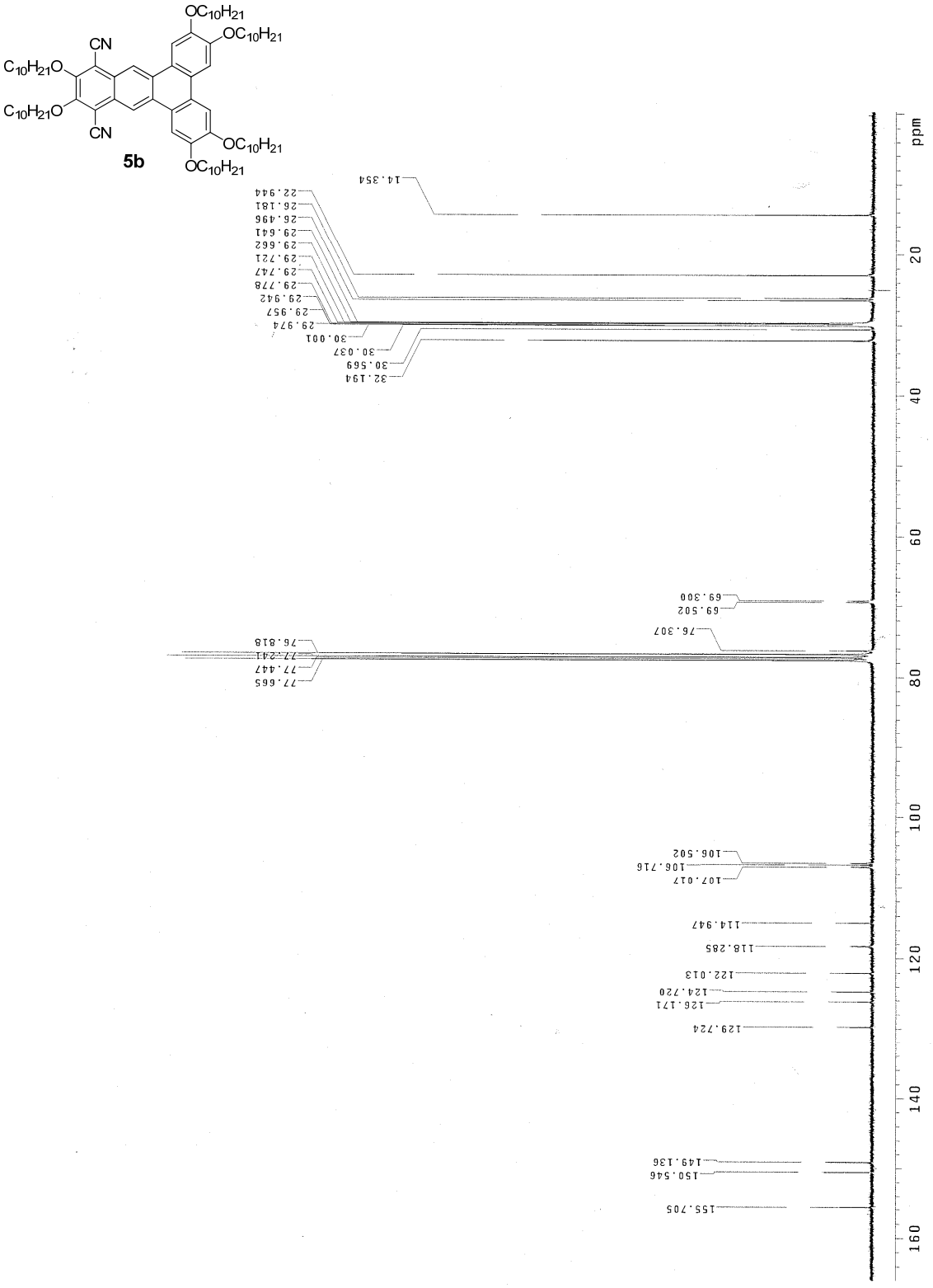
9.65
4.57
2.00
2.08
2.07


OC10H21
OC10H21
CN
C10H21O
C10H21O
CN
OC10H21
OC10H21
5b
14.354
22.944
26.181
26.496
29.641
29.662
29.721
29.747
29.778
29.942
29.957
29.974
30.001
30.037
30.569
32.194
69.300
69.502
76.307
76.818
77.241
77.447
77.665
106.502
106.716
107.017
114.947
118.285
122.013
124.720
126.171
129.724
149.136
150.546
155.705
ppm
20
40
60
80
100
120
140
160